

STUDY IN COMETARY ASTROPHYSICS

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Prepared by

Louis J. Stief & Vincent J. DeCarlo  
Melpar, Inc.  
3000 Arlington Boulevard  
Falls Church, Virginia

# TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
1. NH EMISSION FROM $\text{NH}_3$ AND $\text{N}_2\text{H}_4$ BY VACUUM ULTRAVIOLET PHOTOLYSIS	1
1.1 Introduction	1
1.2 Results	1
1.3 Discussion	2
2. PHOTOLYSIS OF $\text{NH}_3 + \text{CH}_4$ AND $\text{H}_2\text{O} + \text{CH}_4$ MIXTURES	5
2.1 Introduction	5
2.2 Photolysis of $\text{NH}_3$ and $\text{H}_2\text{O}$ with $\text{CH}_4$ , $\lambda < 1450\text{\AA}$	5
2.2.1 Results	6
2.2.2 Discussion	6
2.3 Photolysis of $\text{CH}_4 + \text{H}_2\text{O}$ , $\lambda < 1450\text{\AA}$	6
2.3.1 Results	7
2.3.2 Discussion	8
3. ELECTRON BOMBARDMENT OF LOW TEMPERATURE SOLIDS	9
3.1 Introduction	9
3.2 Results	9
3.3 Discussion	10

## ABSTRACT

Studies have been initiated on NH emission produced from  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  by vacuum ultraviolet photolysis. Strong cometary implications for the presence of  $\text{N}_2\text{H}_4$  as a source of NH has been obtained.

Experiments have continued with the vacuum ultraviolet photolysis of  $\text{NH}_3 + \text{CH}_4$  and  $\text{H}_2\text{O} + \text{CH}_4$ . For these systems quantum yield measurements for production of  $\text{C}_2\text{H}_6$  have been made. In addition, studies with  $\lambda < 1450$  for  $\text{CH}_4 + x\text{H}_2\text{O}$  system at  $-195^\circ\text{C}$  and  $25^\circ\text{C}$  have been carried out and analysis of products shows that in addition to expected products,  $\text{CO}_2$  is produced by some unexplained mechanism.

Electron bombardment experiments have also continued with the measurement of the half life of the excited  $\text{H}_2\text{O}$  molecule at  $-195^\circ\text{C}$ .

Experiments have started with the  $\text{CH}_4 \cdot 6\text{H}_2\text{O}$  system and compounds not readily expected and found to be present are  $\text{CO}_2$  and  $\text{CH}_3\text{COCH}_3$ .

# 1. NH EMISSION FROM $\text{NH}_3$ AND $\text{N}_2\text{H}_4$ BY VACUUM ULTRAVIOLET PHOTOLYSIS

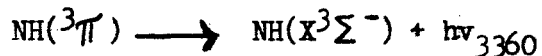
## 1.1 Introduction

There has been wide speculation on the gaseous composition of comets. Spectral information directly related to this problem has been obtained from the large number of free radicals that emit light in the visible by a fluorescence mechanism. Direct information on the nature of the parent compounds is not available but can be obtained in the laboratory by vacuum ultraviolet photolysis at very low pressures. These experiments are expected to find molecules that will produce the free radicals of interest by a simple photodissociation of the molecule.

During this quarter experiments have been carried out for NH emission obtained from  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$ . Strong cometary implications for  $\text{N}_2\text{H}_4$  have been obtained.

## 1.2 Results

Using the identical experimental system and procedure developed for studying  $\text{C}_2$  emission from  $\text{C}_2\text{H}_2$  it has been found that when hydrazine vapor at a pressure of 50u Hg is photolyzed at the Kr resonance lines ( $1165\text{\AA}$  and  $1236\text{\AA}$ ) an emission at  $3360\text{\AA}$  corresponding to the transition



is observed. A weaker emission in region of  $2600\text{\AA}$  is also observed which would be consistent with the transition



Except for OH emission arising from presence of water as an impurity in the hydrazine, no other emissions are observed in the region  $2000\text{\AA}$  to  $7000\text{\AA}$ . Specifically, the  $\text{NH}(c^1\Pi) \longrightarrow \text{NH}(a^1\Delta)$  emission at  $3240\text{\AA}$  is

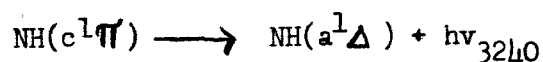
absent in pure hydrazine. This system is observed in emission from  $\text{NH}_3$  at the Kr resonance lines.<sup>1</sup> With continued photolysis of hydrazine however, the  $3240\text{\AA}$  emission is observed and continue to increase with time. It is also observed when hydrazine is used without purification. Both of these results suggest that the  $\text{NH}(c^1\Pi)$  emission arises from photolysis of  $\text{NH}_3$  formed as a product of  $\text{N}_2\text{H}_4$  photolysis or present as an impurity in the hydrazine.

The emission spectrum from hydrazine has been recorded at pressures from  $5\mu$  to  $1.3\text{mm}$  Hg. The maximum intensity of the  $3360\text{\AA}$  emission occurred at  $50\mu$  Hg.

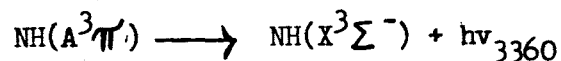
When hydrazine is photolyzed at the Xe resonance line ( $1470\text{\AA}$  and  $1295\text{\AA}$ ), no emissions are observed in the region  $2000\text{--}7000\text{\AA}$ .

### 1.3 Discussion

Emission spectra of  $\text{NH}_2$  and  $\text{NH}$  observed in comets has been generally attributed to dissociation of ammonia to form the radicals in question. However, vacuum ultraviolet photolysis of  $\text{NH}_3$  results in emission<sup>1</sup> at  $3240\text{\AA}$



while the cometary emission at  $3360\text{\AA}$  corresponds to



Emission at  $3360\text{\AA}$  from  $\text{NH}$  in the comet by means of a fluorescence mechanism requires the eventual presence of  $\text{NH}$  in the ground ( $X^3\Sigma^-$ ) state. The  $a^1\Delta \longrightarrow X^3\Sigma^-$  transition is highly forbidden and any  $\text{NH}(a^1\Delta)$  would therefore have a very long lifetime. Thus the transition  $c^1\Pi \longrightarrow a^1\Delta$

1. K. H. Becker and K. H. Welge, Z. Naturforsch. 18a, 600 (1963).

should be observed in comets along with the  $A^3\Pi \longrightarrow X^3\Sigma^-$ . Since this is not observed,  $N_2H_4$  which leads to the production of NH in the triplet system appears to be more important for NH production in cometary atmospheres than  $NH_3$  which leads to NH in the singlet system.

Based on the heats of formation given in table 1 and energies of the states of NH above the  $X^3\Sigma^-$  ground state given in table 2, the energetics of several plausible elementary reactions have been calculated (table 3). Reactions leading to ground state NH and  $NH_2$  radicals (1, 2, and 5) are energetically possible at all wavelengths employed. Formation of  $NH(d^1\Sigma^+)$  (4 and 7) is energetically impossible at even the shortest wavelength (1165 $\text{\AA}$  Kr line) used in these experiments. Thus either the identification of the emission in region of 2600 $\text{\AA}$  with production of  $NH(d^1\Sigma^+)$  is wrong or the calculated  $\Delta H$  is in error by at least 32 kcal/mole. No further evidence is presently available at this time to enable a choice to be made between the two alternatives. Formation of  $NH(A^3\Pi)$  which leads to the observed emission at 3360 $\text{\AA}$  may occur by reaction 3 or reaction 6. Since, according to the available value for heats of formation, reaction 6 is energetically possible at the 1165 $\text{\AA}$  Kr line but not at the 1236 $\text{\AA}$  Kr line, the occurrence of 6 requires that insertion of a  $CaF_2$  filter (eliminating the 1165 $\text{\AA}$  line but transmitting 30% of the 1236 $\text{\AA}$  line) should completely eliminate the 3360 $\text{\AA}$  emission. The fact that the emission is reduced by 30% under these conditions may be taken as evidence that reaction 3 is the more important source of  $NH(A^3\Pi)$ .

Table 1

## Heats of Formation

Molecule	$\Delta H_f$ (kcal/mole)
$N_2H_4$	-11
$NH_3$	22.7
$NH(X^3\Sigma^-)$	83
$NH_2$	41
H	52

Table 2

## Energies of States

State	kcal/mole
$NH(X^3\Sigma^-)$	0
$NH(A^3\Pi)$	85
$NH(d^1\Sigma^+)$	228

Table 3

## Energetics of Elementary Reactions

Reaction	$\Delta H$ (kcal/mole)	Wavelength Below Which Process is Energetically Possible
(1) $N_2H_4 \longrightarrow 2NH_2$	59	4844 $\overset{\circ}{A}$
(2) $N_2H_4 \longrightarrow NH(X^3\Sigma^-) + NH_3$	49	5833 $\overset{\circ}{A}$
(3) $N_2H_4 \longrightarrow NH(A^3\Pi) + NH_3$	134	2133 $\overset{\circ}{A}$
(4) $N_2H_4 \longrightarrow NH(d^1\Sigma^+) + NH_3$	277	1032 $\overset{\circ}{A}$
(5) $N_2H_4 \longrightarrow NH(X^3\Sigma^-) + NH_2 + H$	153	1868 $\overset{\circ}{A}$
(6) $N_2H_4 \longrightarrow HN(A^3\Pi) + NH_2 + H$	238	1201 $\overset{\circ}{A}$
(7) $N_2H_4 \longrightarrow NH(d^1\Sigma^+) + NH_3$	381	750 $\overset{\circ}{A}$

## 2. PHOTOLYSIS OF $\text{NH}_3 + \text{CH}_4$ AND $\text{H}_2\text{O} + \text{CH}_4$ MIXTURES

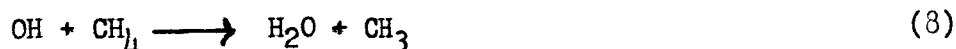
### 2.1 Introduction

These studies were initiated to develop (a) an understanding of free radical reactions that could occur in the nucleus of a comet, or in the gas phase immediate to the surface of the nucleus and (b) information concerning which intermediates and stable molecules are important in a cometary nucleus. The present series of experiments will investigate all the radicals and reactions that can be produced from mixtures of  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  at  $25^\circ\text{C}$  and  $-195^\circ\text{C}$ . It has been possible to produce the OH and  $\text{NH}_2$  radical from  $\text{H}_2\text{O}$  and  $\text{NH}_3$  respectively at  $25^\circ\text{C}$  with  $\lambda > 1450\text{\AA}$ , but with the shift in absorption at  $-195^\circ\text{C}$   $\lambda < 1450$  was required for dissociation of these molecules.

Quantum yield measurements have been made for reactions of  $\text{NH}_2 + \text{CH}_4$  and  $\text{OH} + \text{CH}_4$  at  $25^\circ\text{C}$  for  $\lambda > 1450\text{\AA}$ . In addition, extensive experiments have been carried out at  $25^\circ$  and  $-195^\circ\text{C}$  with  $\text{CH}_4 + \text{H}_2\text{O}$  with  $\lambda < 1450$ .

### 2.2 Photolysis of $\text{NH}_3$ and $\text{H}_2\text{O}$ with $\text{CH}_4$ , $\lambda > 1450\text{\AA}$

The reactions that occur in these systems were discussed in the last report and are summarized as follows:



During this quarter the quantum yield for ethane production was determined for both systems at the pressure of methane required for optimum production of ethane. The same experimental system and procedure described in the last report were used.



### 2.2.1 Results

Since the rate of ethane production decreases with time, rates were determined from initial slopes of ethane vs. photolysis time plots. It was found that for the system  $\text{H}_2\text{O}-\text{CH}_4$ ,  $\phi_{\text{C}_2\text{H}_6} = 0.6$ , and for the system  $\text{NH}_3-\text{CH}_4$ ,  $\phi_{\text{C}_2\text{H}_6} = 0.2$ .

### 2.2.2 Discussion

These results suggest that in the  $\text{H}_2\text{O}-\text{CH}_4$  system, only reactions 8 and 10 are occurring. The low value for the quantum yield for ethane production in the  $\text{NH}_3-\text{CH}_4$  system indicates that in addition to the occurrence of reactions 9 and 10,  $\text{NH}_2$  radicals are disappearing by combination, possibly to form hydrazine.



No further analysis of products has been made for these systems.

### 2.3 Photolysis of $\text{CH}_4 + \text{H}_2\text{O}$ , $\lambda < 1450\text{\AA}$

Methane, water and ammonia have important cometary significance and any radical-molecule reactions they can undergo would have strong implications on cometary structure. The original experiments with  $\lambda < 1450$  were to study the  $\text{NH}_2$  and  $\text{OH}$  radical from ammonia and water respectively with the methane molecule. This was successful at room temperature but was not possible at  $-195^\circ\text{C}$  due to the shift in absorption<sup>2</sup> at lower temperature. To initiate reaction, experiments were carried out with methane-water mixtures at  $-195^\circ\text{C}$  using Kr lamps with  $\lambda = 1165$  and  $1236\text{\AA}$ . Under these conditions both compounds are capable of absorbing the incident photons which makes the kinetics of the reaction difficult to interpret.

2. K. Dressler and O. Schnepp, J. Chem. Phys. 33, 270 (1960).

### 2.3.1 Results

Since the hydrate system  $\text{CH}_4 \cdot 6\text{H}_2\text{O}$  has been proposed<sup>3</sup> as a means of having a low vapor pressure of  $\text{CH}_4$  at relatively high temperatures, the photolysis of this system has been studied for free radical production and reaction. The products obtained from this mixture are  $\text{CO}_2$ ,  $\text{C}_2\text{H}_6$ , and  $\text{H}_2$ . The amount of products obtained was small and efforts were made to increase the yield of products by increasing the photolysis time, increasing the size of the deposit and varying the mode of deposition where the surface was periodically renewed with a fresh mixture of  $\text{CH}_4 + 6\text{H}_2\text{O}$ . These approaches were not successful in increasing the amounts of products or in changing their distribution. The distribution was changed however when the  $\text{H}_2\text{O}/\text{CH}_4$  ratio was varied. To correlate the results at  $-195^\circ\text{C}$  some gas phase work has been carried out investigating the effect of the  $\text{H}_2\text{O}/\text{CH}_4$  ratio and the potential fluorescence of a new molecule or fragment in this system.

Photolysis of  $\text{CD}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{CH}_4 \cdot 6\text{D}_2\text{O}$  in the solid results in the detection of  $\text{D}_2$  and  $\text{H}_2$  respectively in the gas phase above the solid. Evidently, the hydrogen is being produced from the methane and is diffusing out of the solid. Because of the unexpected  $\text{CO}_2$ , great care was taken to purify the starting materials. Consistent results have been obtained on the ratio  $\text{CO}_2/\text{C}_2\text{H}_6$  as a function of the ratio  $\text{H}_2\text{O}/\text{CH}_4$  and these are presented in Table 4. The ratio of the products was found to be a linear function of the ratio of the reactants with intercept at origin.

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3. D. H. Robey, Journal of the British Interplanetary Society 17, 205 (1959-60).

TABLE 4

Ratio of Reactants	Ratio of Products
$\frac{\text{H}_2\text{O}}{\text{CH}_4}$	$\frac{\text{CO}_2}{\text{C}_2\text{H}_6}$
6	$0.4 \pm 0.1$
12	0.8
18	$1.2 \pm 0.1$
72	$5.0 \pm 0.5$

In the gas phase at 25°C, photolysis of a mixture of 18mm H<sub>2</sub>O and 3mm CH<sub>4</sub> in a reaction volume of approximately 300cc resulted in the formation of equal amounts of CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>. The amount of CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> formed was about ten times that formed in same time for photolysis of same amount of the reactants deposited at -196°C. In the photolysis of 18mm H<sub>2</sub>O with 1.5mm and 1mm CH<sub>4</sub> respectively, ethane was not observed as a product although CO<sub>2</sub> was still formed. Ethane amounting to as little as 2-3% of the CO<sub>2</sub> could have been easily detected. In the fluorescence experiments with this system we did not detect any new emissions and observed only the strong OH emission.

### 2.3.2 Discussion

The most significant result of this series of experiments is the production of CO<sub>2</sub> at -195°C and at 25°C for the mixture CH<sub>4</sub> + xH<sub>2</sub>O. In the gas phase with  $\lambda > 1450$  no CO<sub>2</sub> was observed when the reactive species were OH and H. Therefore at  $\lambda < 1450$ , the reaction must involve some combination of CH<sub>4</sub>, H<sub>2</sub>O, OH, O and CH<sub>2</sub> since these are available at this wavelength.

There is no other evidence of the potential mechanism since intermediates such as HCHO or CO have not been detected. Since the reaction occurs at  $-195^{\circ}\text{C}$  it is necessary that the reaction have an activation energy less than 5 kcal.

Whatever the reaction involved, it is evident that both  $\text{CO}_2$  and  $\text{C}_2\text{H}_6$  are formed in competitive reactions possibly involving the methylene radical. Formation of  $\text{C}_2\text{H}_6$  is evidently favored over  $\text{CO}_2$  formation in the gas phase since a ratio of  $6\text{H}_2\text{O}$  to  $1\text{CH}_4$  is required to form equal amounts of  $\text{CO}_2$  and  $\text{C}_2\text{H}_6$ . In the solid phase, formation of  $\text{C}_2\text{H}_6$  is even more favorable as compared to  $\text{CO}_2$  formation since a ratio of  $18\text{H}_2\text{O}$  to  $1\text{CH}_4$  is required to form equal amounts of  $\text{CO}_2$  and  $\text{C}_2\text{H}_6$ . This may be a measure of the complexity of the reaction leading to  $\text{CO}_2$  since a more complex mode of reaction may be expected to be more effected by change of phase than a simple one step process.

### 3. ELECTRON BOMBARDMENT OF LOW TEMPERATURE SOLIDS

#### 3.1 Introduction

To evaluate the role of cosmic radiation, i.e., chemical reactions, production of active species, etc., in cometary phenomena, the effect of charged particles (electrons or protons) on low temperature solids ( $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ , etc.) is of interest.

Experiments have continued with  $\text{H}_2\text{O}$  at  $-195^{\circ}\text{C}$  and initial experiments have been carried out for  $\text{CH}_4 \cdot 6\text{H}_2\text{O}$  system at  $-195^{\circ}\text{C}$ .

#### 3.2 Results

Half life measurements of 200 msec have been made for  $\text{H}_2\text{O}$  at  $-195^{\circ}\text{C}$  using the experimental system described in the last quarterly report.

This value was obtained by a photographic recording of the photometer output displayed on a scope. The decay of the emission could be followed up to twice the half life and was found to be logarithmic within this interval.

Preliminary experiments have been carried out for chemical reactions induced in the  $\text{CH}_4^+\text{H}_2\text{O}$  system<sup>3</sup> by bombarding with 5 Kev electrons. Analysis of the products has not been completed but positive identification has been made for  $\text{CO}_2$  and  $\text{C}_2\text{H}_6$ , very good evidence exists for the production of  $\text{CH}_3\text{COCH}_3$  and other possible compounds are  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ .

Experiments were carried out from 15 minutes to 2 hours. These runs have shown that 15 minutes is sufficient to obtain measurable products with pulsed beam intensities of  $6.6 \times 10^{10}$  electrons/sec/cm<sup>2</sup> of 1 msec duration.

### 3.3 Discussion

These experiments have shown that new compounds can be produced from the  $\text{CH}_4^+\text{H}_2\text{O}$  system under electron bombardment. The  $\text{CO}_2/\text{C}_2\text{H}_6$  ratio was found to be 0.7 and accounted for 80% of the products. Evidence is available for the production of  $\text{CH}_3\text{COCH}_3$  at the longer bombardment experiments. Further analysis of the mass spectral cracking patterns is necessary before  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  can be identified positively.

The products normally obtained from  $\text{CH}_4^+$  radiation<sup>4</sup> are  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$  and  $\text{C}_2\text{H}_4$ . No evidence for production of  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$  has been obtained in these experiments.

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4. L. W. Sieck and R. H. Johnsen, J. Phys. Chem. 67, 2281 (1963).